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A detailed atomistic molecular mechanics model has been developed for the polycarbonate of bisphenol-A (PC) and is employed here to generate dense (glassy) microstructures. The resulting microstructures are being used to investigate the inelastic behavior of PC. The phenylene ring flip is a feature of PC which has been widely studied using various NMR techniques. It is the simplest of inelastic processes and is amenable for simulation and study. The energy barrier to the ring flip has been obtained using the minimized structures, and the calculated mean energy barrier is 10.4 ($\pm$6.0) Kcal/mole. This value agrees very well with the NMR results that have been reported. [illegible]

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Paper number as listed on program _____

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[C] AUTHORS (Underline name of speaker)	[D] Business Mailing Address Including Zip Code and telephone Number (List Address only once if all authors at same address.)	[E] ACS Member?	Division Member?	[F] American Chemist or Chemical Engineer? (If not, give classification such as biologist, physicist, etc. Ph.D?)
M. Hutnik A.S. Argon U.W. Suter	Massachusetts Institute of Technology 77 Massachusetts Ave. Room 1-306 Cambridge, MA 02139	☒ Yes ☐ No	☒ Yes ☐ No	☐ Chemist ☐ Chemical Engineer Other Materials Scientist

NOTE: All presenting authors must register for the meeting –either full meeting registration or one-day registration for the day of presentation.

[G] Work done at M.I.T.

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MOLECULAR STRUCTURE OF AMORPHOUS BISPHENOL-A POLYCARBONATE. M. Hutnik*, A. S. Argon*, and U. W. Suter**, (*)Massachusetts Institute of Technology Cambridge,MA 02139, (**)Institut fuer Polymere, ETH-Zuerich, CH-8092 Zuerich, Switzerland.

A detailed atomistic molecular mechanics model has been developed for the polycarbonate of bisphenol-A (PC) and is employed here to generate dense (glassy) microstructures. The resulting microstructures are being used to investigate the inelastic behavior of PC. The phenylene ring flip is a feature of PC which has been widely studied using various NMR techniques. It is the simplest of inelastic processes and is amenable for simulation and study. The energy barrier to the ring flip has been obtained using the minimized structures, and the calculated mean energy barrier is 10.4 (± 6.0) Kcal/mole. This value agrees very well with the NMR results that have been reported.

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MOLECULAR STRUCTURE OF AMORPHOUS BISPHENOL-A POLYCARBONATE

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INTRODUCTION

A detailed atomistic molecular mechanics model has been developed for the polycarbonate of bisphenol-A (PC). The technique used has been successfully applied earlier to simple vinyl polymers and is employed here to generate dense (glassy) packing of PC [1,2]. The resulting microstructures are being used to investigate the inelastic behavior of PC. The first such application is the phenylene ring flip which occurs in glassy PC. The ring flip is a feature of PC which has been widely studied using various NMR techniques [3,4] and as the simplest of inelastic processes is amenable for simulation and study using the generated microstructures.

MODEL

To be able to model PC, it is necessary to first understand the intramolecular interactions of the PC repeat unit. We developed a molecular mechanics force field of the PC repeat unit that is appropriate for the microstructure generation technique, based on fixed bond angles and bond lengths. A Lennard-Jones potential energy function was used to represent the Van der Waals interatomic interactions while the Coulombic interactions are represented as a truncated Block-Walker potential [2,5]. Intrinsic torsional potentials specific to PC were constructed and are included in the force field. The details of the force field will be described in full at a future time.

Amorphous PC microstructures were generated using the above force field and the modelling technique developed by Theodorou and Suter [1]. The model is static, with temperature only entering in the choice of the density, and includes spatially periodic continuation. The periodic cube edge length is 18.44 Angstroms, the degree of polymerization is 17, and the density is 1.20 g/cm^3, which is the experimental value at 298 K.

Initial chain conformations of the microstructures were generated using a Monte Carlo technique with the rotational isomeric state scheme previously developed for PC [6]. A staged energy minimization procedure is then applied to the microstructure to obtain well relaxed, amorphous systems (Figure 1, hydrogens are omitted for clarity). No vestiges of crystallinity are observed. The energy minimization for PC is not straight forward, requiring approximately 30 stages in which the atomic radii and the partial point charges are gradually 'blown up'. The difficulty of the minimization is due to the size of the rigid moiety in the PC repeat unit. 12 minimized microstructures have been generated so far.

SIMULATION OF RING FLIP

The phenylene ring flip that occurs in PC has been a topic of intense experimental investigation using various NMR techniques [3,4]. The energy barrier of the ring flip is due to a combination of both intra- and intermolecular interactions. Since glass densities are very high, the intermolecular contributions are high and could potentially dominate the energy barrier. Using the minimized PC microstructures it is possible to obtain this barrier and compare the results with the reported experimental values.

To calculate the energy barrier to ring flip, a phenylene ring is incrementally rotated and then 'fixed' while the rest of the structure is allowed to relax. This process is repeated until a 'flip' is performed in the laboratory reference frame. Every ring of one microstructure is treated so that a sufficient statistical sample is obtained and possible spatial effects can be studied.

RESULTS AND DISCUSSION

A typical rotation path is displayed in Figure 2. It shows the system potential energy vs. torsional angle (true rotation in parentheses) for the third ring along the chain. The true rotation is defined as the angle between the plane of the ring at the onset of the experiment and the plane of the ring at present. Figures 3 and 4 show the microstructure (hydrogens are omitted and the atomic radii are shrunk so that the rotation is easily visible) at two different points along the rotation path; Figure 3 contains the initial configuration of the chain (torsional angle=57°, true rotation=0°), and Figure 4 gives the configuration at the peak energy (torsional angle=117°, true rotation =55°).

In general for the ring flip, preceding the initial energy peak the conformational changes that occur as the structure relaxes are reversible, whereas the conformational changes are irreversible after the energy peaks. This corresponds to the unrestrained relaxation from a saddle point configuration in transition state theory.

The results of the ring flip calculations are as follows (value in parenthesis is standard deviation of the mean):

34 barriers calculated
mean energy barrier = 10.4 (±6.0) Kcal/mole

The frequency distribution of the calculated results of the ring flip are shown in Figure 5.

These results compare very favorably to the NMR results that have been calculated:

- Proton spin-lattice relaxation:
  12 Kcal/mole [3]

- Dipolar Rotational Spin-Echo ^{13}C NMR:
  11 Kcal/mole [4]

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(5) Block, H.; Walker, S. M. Chem. Phys. Let. 1973, 19, 363.
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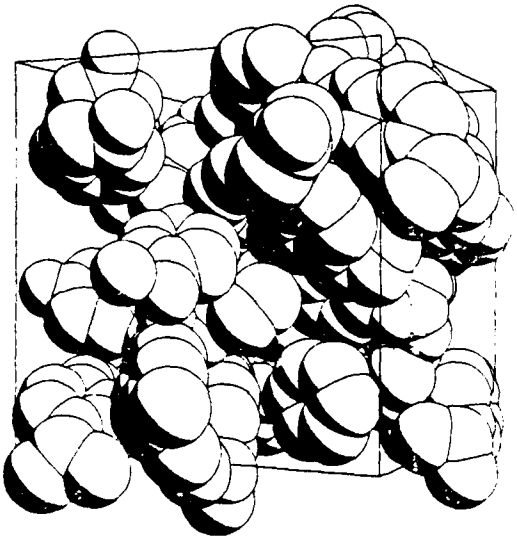

Figure 1. Periodic cube of PC, hydrogens omitted for clarity.

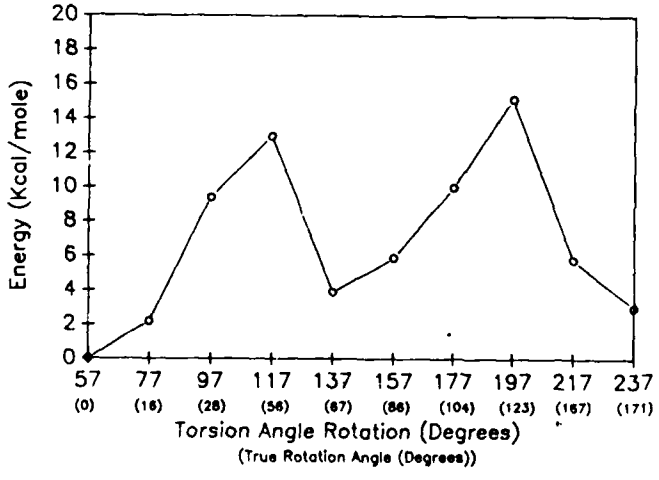

Figure 2. Ring flip rotation path for the third ring along the chain.

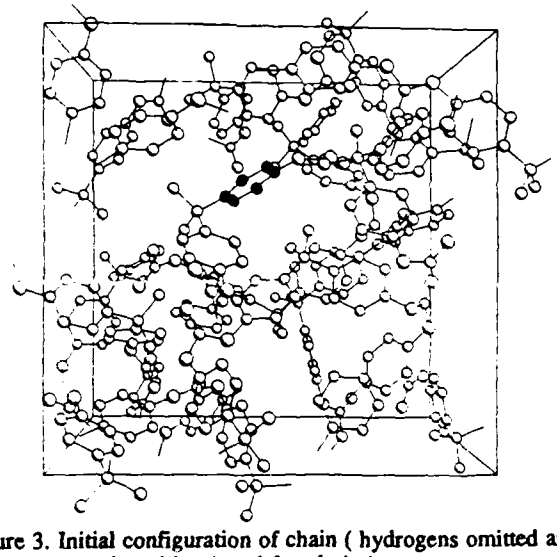

Figure 3. Initial configuration of chain (hydrogens omitted and atomic radii reduced for clarity), torsional angle = 57°, true rotation = 0°.

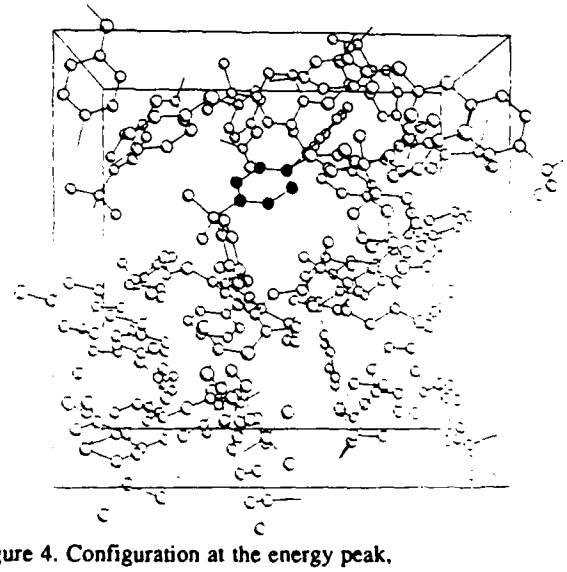

Figure 4. Configuration at the energy peak, torsional angle =117°, true rotation = 55°.

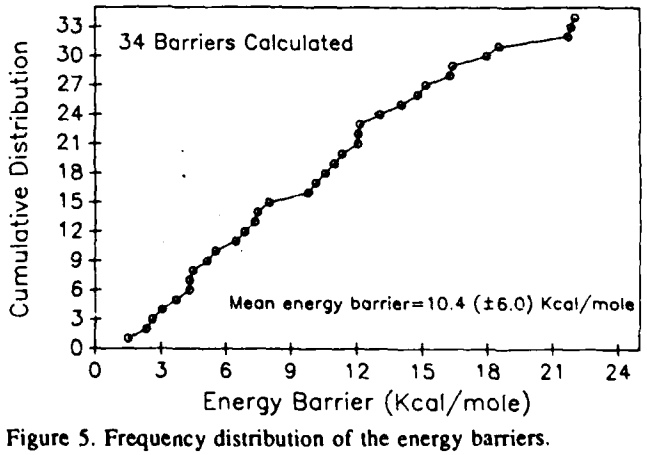

Figure 5. Frequency distribution of the energy barriers.